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CORROSION OF CHROMIUM-NICKEL STAINLESS STEEL IN LITHIUM

by

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12

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ABSTRACT: Three series of 1Kh18N9T stainless-steel specimens were tested for corrosion behavior in lithium at 700C for 10 or 200 hr. Series 1 and 2 specimens were tested in lithium containing a small amount of C¹⁴ isotope and in tanks made of 1Kh18N9T steel (series 1) or Armco-iron (series 2). In the case of series 3 specimens, the lithium contained 0.1% carbon in addition to C¹⁴ and the tanks were made of Armco-iron. The corrosion was found to follow the same pattern under all the conditions tested, and was characterized by a gradual dissolution of chromium and nickel from the surface layer of the specimens. With decreasing chromium and nickel content the steel changes its structure and gradually loses its corrosion resistance. Microporosity formed in points previously occupied by chromium and nickel lowers considerably the steel ductility. The carbon content in lithium and tank material were found to have a marked effect on the intensity of processes associated with corrosion. The most intensive loss of chromium and nickel was observed in series 2 and 3 specimens in which in 200 hr the chromium content in the surface layer dropped by 50% and the nickel content, by 45 and 50% of the original content, respectively. Specimens of series 1 under the same conditions lost 10% of their chromium and 30% of their nickel. Accordingly, the elongation of the series 1, 2, and 3 specimens dropped from the original 48.2% to 47.1, 26.4, and 24.4%, respectively. Carbon contained in lithium was found to diffuse into the steel. However, in the first hours of the test, carbon concentrates primarily in the surface layer. As the chromium content in the surface layer drops, carbon migrates inside, following the front of original chromium content. Orig. art. has: 7 figures and 4 tables. English translation: 7 pages.

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѐ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

CORROSION OF CHROMIUM-NICKEL STAINLESS STEEL IN LITHIUM

N. M. Beskorovaynyy, V. K. Ivanov, and V. V. Petrashko

Possibility of application of austenitic chromium-nickel steels as structural material for work in contact with liquid lithium is limited, since these steels possess unsatisfactory corrosion resistance [1]. In connection with this it is expedient to study the cause of low corrosion resistance of chromium-nickel steels in lithium.

In this work there are brought out results of tests in lithium of [1Kh18N9T] (1X18H9T) steel in reaction beakers from this steel and from Armco iron. Into lithium there was introduced radioactive isotope C^{14} , quantity of which did not essentially change the overall content of carbon in lithium; in a number of experiments there was used lithium with considerable additions of carbon (Table 1).

Table 1. Conditions of Testing of 1Kh18N9T Steel in Lithium

Variant of experiment	Material of reaction beakers	Additions to lithium
I	1Kh18N9T	Radioactive isotope C^{14}
II	Armco Iron	The same
III	" "	Radioactive isotope C^{14} and 0.1% C (graphite)

Corrosion tests were conducted in static conditions at temperature 700°C for 10 and 200 h. Then samples were investigated by method of laminar analysis. Concentration of chromium was determined by method flame photometry [2], and concentration of nickel — by means of spectral analysis.

On Fig. 1 there are presented distribution curves of chromium and nickel in 1Kh18N9T steel after testing in lithium, which indicates lowering of chromium and nickel content in surface layer. In contrast to distribution curves of chromium, distribution curves of nickel have complicated character with maximum and minimum, position of which is changed depending upon time and testing conditions.

The least change of composition occurs when the sample and reaction beaker are from one material, since lithium is saturated with chromium and nickel simultaneously from the sample and beaker (Table 2).

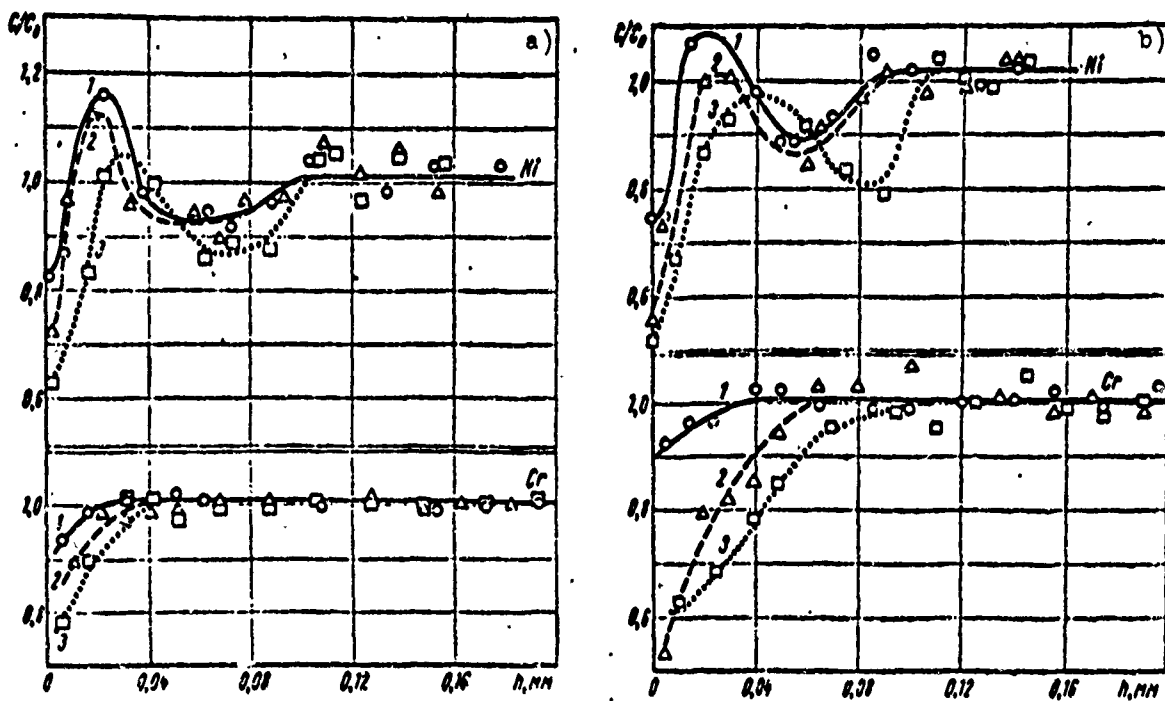


Fig. 1. Distribution of chromium and nickel in 1Kh18N9T steel after testing in lithium at 700°C for 10 h (a) and 200 h (b) with respect to first (1) second (2) and third (3) variants.

Table 2. Change of Content of Chromium and Nickel on Surface of 1Kh18N9T Steel

Variant of experiment	Content of Cr, % by weight		Content of Ni, % by weight	
	in 10 h	in 200 h	in 10 h	in 200 h
I	0.9	0.9	0.8	0.7
II	0.85	0.5	0.7	0.55
III	0.8	0.5	0.6	0.5

More significant changes in 1Kh18N9T steel occur after testing in reaction beakers from Armco iron (II and III variants). Chromium and nickel will form solid solutions with iron, therefore in the process of testing atoms of chromium and nickel, dissolved in lithium, can be transferred to iron, and their concentration in lithium will be reduced. This circumstance leads to acceleration of processes of dissolution of chromium and nickel from surface layer of samples (see Fig. 1), which is also indicated by change of increase of weight of samples — positive in I variant of testing and negative in II and III variants (Fig. 2). Analogous results were observed during tests of chromium stainless steels [3].

Thus, testing conditions of 1Kh18N9T steel in II and III variants of experiment with the same character of corrosion process are more rigid as compared to I variant and due to mass transfer from sample to reaction beaker to a certain degree there are simulated actual work conditions of structural materials in liquid-metal heat-transfer agents, when because of temperature gradient there occurs mass transfer from hot zone to cold.

Results of tests indicate the significant effect of carbon on lowering of content of chromium and nickel in surface layer of 1Kh18N9T steel. With higher content of carbon in lithium the corrosion processes go more intensively.

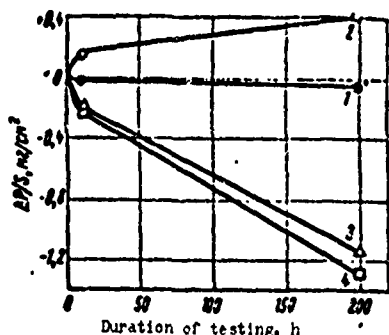


Fig. 2. Change of weight of 1Kh18N9T steel after testing at 700°C in argon 1 - and in lithium according to first 2 - second 3 - and third 4 - variants.

In II variant the carbon content in lithium composed approximately 0.1%, since carbon entered lithium from iron reaction beakers. In III variant lithium contained about 0.2% carbon, since 0.1% carbon was additionally introduced into it in the form of graphite.

Application of radioactive isotope C^{14} makes it possible to investigate the behavior of carbon during corrosion of chromium-nickel steel in lithium. After 10 h testing according to I variant (samples and beakers of 1Kh18N9T steel) the surface layer has high radioactivity (Fig. 3a and Table 3) with simultaneous significant increase of microhardness (Fig. 4a) and minimum change of composition of surface layer with respect to chromium and nickel. From this it follows that with small decrease of content of chromium the carbon is transferred from lithium to surface of sample, since chromium has higher chemical affinity to carbon than lithium, and microhardness of this layer is increased probably as a result of carbide formation (Fig. 5).

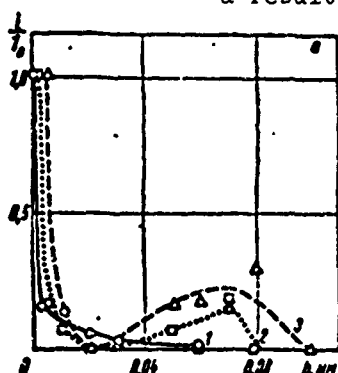


Fig. 3. Distribution of radiocarbon in 1Kh18N9T steel after testing in lithium, containing isotope C^{14} , at temperature 700°C for 10 h a) and 200 h b) according to first 1 - second 2 - and third 3 - variants.

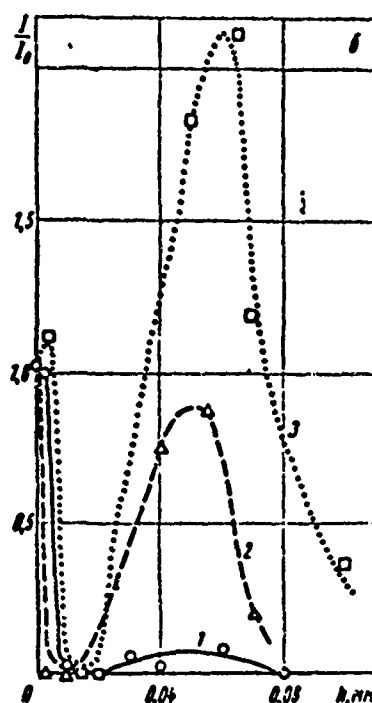


Table 3. Radioactivity of Surface of 1Kh18N9T Steel at Different Variants of Testing, Referred to Radioactivity of Surface of Sample Tested According to I Variant for 10 h

Duration of testing, h	Variant of experiment		
	I	II	III
10	1.0	0.08	0.05
200	0.16	0.01	0.02

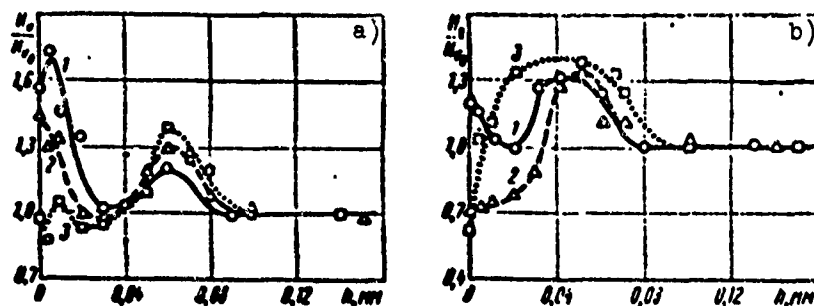


Fig. 4. Distribution of microhardness in 1Kh18N9T steel after testing in lithium at 700°C for 10 h (a) and 200 h (b) according to first (1) second (2) and third (3) variants.

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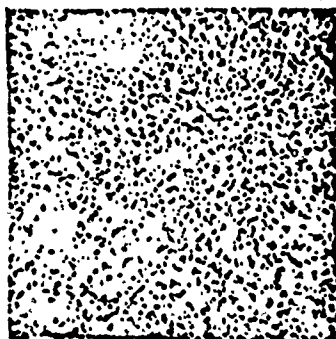


Fig. 5. Surface of 1Kh18N9T steel after testing in lithium at 700°C for 10 h according to I variant ($\times 1350$).

With increase of duration of testing to 200 h both radioactivity and microhardness of surface are noticeably reduced (Fig. 3b and Table 3, Fig. 4b), which by analogy with chromium steels should indicate both some lowering of chromium content and decrease of quantity of carbide phase on surface [3]. Redistribution of carbon occurs simultaneously. Maximum radioactivity still is preserved on surface, but then there follows the zone where radiocarbon is absent. This zone is disposed at the same depth as maximum on distribution curve of nickel. Further, at a depth about 0.06 mm there is again marked maximum on distribution curve of carbon (Fig. 3b) and maximum on microhardness curve corresponds to it (Fig. 4b). At this depth the concentration of chromium is approximately equal to initial, and on distribution curve of nickel there is minimum.

With contamination of lithium by carbon (II and III variants) lowering of content of chromium and nickel in surface layer of 1Kh18N9T steel goes more intensively, but form of distribution curves of chromium and nickel (see Fig. 1) is kept. However, distribution of carbon is changed significantly. On the surface the carbon content is reduced to small concentrations (see Table 3). In the zone where maximum is located on distribution curve of nickel, carbon is absent after 10 h and 200 h of testing. In the zone of minimum, conversely, concentration of carbon increases with increase of carbon content in lithium, especially with increase of duration of testing to 200 h. Redistribution of carbon is accompanied by change of microhardness. On the surface the microhardness is significantly reduced, but increases in zone where there is noted maximum of concentration of carbon.

These data indicate that carbon, just as during test of chromium steels, shifts to deeper zones in proportion to how content of chromium is reduced on surface. Such shift is caused by higher chemical affinity of carbon to chromium as compared to nickel, iron, and lithium.

Change of composition of austenitic chromium-nickel steel as a result of surface processes, developing at contact with lithium, is accompanied by change of structure. Layers of sample adjacent to surface do not contain carbides and have raised etchability (Fig. 6). If the structure of austenitic steel is usually revealed when etching in reagent $50\% \text{HCl} + 50\% \text{H}_2\text{O}_2$, then after testing in lithium the structure of subsurface layers is etched instantly in 5% solution HNO_3 in alcohol, i.e., in this zone austenitic chromium-nickel steel loses its acid-resisting properties. In layers with raised etchability there are observed pores, located basically along grain boundaries.

With intense change of composition and structure of surface layers (II and III variants) the plasticity of 1Kh18N9T steel is noticeably reduced (Table 4).



GRAPHIC NOT REPRODUCIBLE

Fig. 6. Microstructure of 1Kh18N9T steel after testing in lithium at 700°C for 200 h according to II variant at a depth of 0.06 mm. Etching agent - 5% solution HNO₃ in alcohol (x1350).

From given data it follows that the most significant process, which causes corrosional destruction of chromium-nickel steels at contact with lithium, is lowering of content of chromium and nickel in surface layer, accompanied by change of structure and appearance of microporosity.

When testing 1Kh18N9T steel in beakers from the same material (I variant) these processes are developed weakly. As a result the composition and structure of surface zone are changed little and, consequently, strength and plasticity of steel are preserved at the level of mechanical characteristics after testing in argon with these same temperature conditions.

After testing 1Kh18N9T steel in beakers from Armco iron and with additional introduction of carbon to lithium (II and III variants) the surface zone is significantly depleted by chromium and nickel, and depending upon degree of depletion the structure is changed and plastic properties of 1Kh18N9T steel are lost.

Lowering of plastic properties during test according to II and III variants is also possible due to carbides, which can be formed during diffusion of carbon from lithium into steel.

Table 4. Change of Mechanical Properties of 1Kh18N9T Steel after Testing in Lithium

Testing conditions	σ_B , kg/mm ²		δ , %	
	10 h	200 h	10 h	200 h
In atmosphere of argon	67.4	67.8	46.2	48.2
I variant	67.1	66.6	46.0	47.1
II "	69.8	69.4	44.8	26.4
III "	69.7	67.6	43.3	24.4

However, main cause of impairment of mechanical characteristics of chromium-nickel steel should be considered those changes of structure, which are due to lowering of content of chromium and nickel in surface layer. Impurities of carbon in lithium only strengthen this process. This is indicated by the following experiment.

Samples of 1Kh18N9T steel were tested in reaction beakers from Armco iron, preliminarily decarbonized in lithium. In this case lowering of content of chromium and nickel occurs more intensively than in I variant, as a result of transfer of atoms of chromium and nickel to iron beaker, and at the same time the effect of carbon on processes of corrosion is excluded to a maximum degree. After 10 h of testing 1Kh18N9T steel had the following mechanical properties: $\sigma_B = 67.3$ kg/mm², $\delta = 47.7\%$, i.e., plasticity was approximately the same value as during test according to I variant. After 200 h of testing the strength of steel composed $\sigma_B = 68.1$ kg/mm², and plasticity - 31.8%. Thus, after 200 h of testing in preliminarily decarbonized iron beaker the plasticity of 1Kh18N9T steel has intermediate value between plasticity during test according to I variant and plasticity during test by II variant.

It is possible to try to explain data obtained during test of chromium-nickel 1Kh18N9T steel in lithium on the basis of concepts on vacancy mechanism of diffusion in alloys based on iron [4], leading to development of pore formation and a number of processes accompanying it.

Dissolution in lithium of atoms of chromium and nickel, and also to some degree atoms of iron, should lead to formation of vacancies on surface of samples of 1Kh18N9T steel. Formed vacancies partially withdraw outside the sample, and partially diffuse deep. In subsurface layers there is possible supersaturation by vacancies above the equilibrium value determined by composition of alloy and temperature. In process of pore formation the alloy passes into more equilibrium state [5].

Presence in sample of a porous region, confirmed by raised etchability and microstructure, can significantly change the distribution of components of alloy with respect to depth of sample.

In porous region there is facilitated diffusion segregation of components of alloy: for example, in subsurface zone of 1Kh18N9T steel, tested in lithium, there is observed raised concentration of nickel, determined by maxima on distribution curves of nickel (see Fig. 1).

Inasmuch as nickel in contrast to chromium is a graphite forming element, then carbon is absent in zones enriched by atoms of nickel. It diffuses into deeper layers, from which nickel departed (minima on distribution curves of nickel). In these layers there is possible some supersaturation of steel by vacancies due to departed atoms of nickel, and in connection with this there are created favorable conditions for formation of chromium carbides. This is indicated by maxima on distribution curves of radiocarbon, and also on curves of microhardness (see Fig. 4). With increase of duration of testing to 200 h the redistribution of components of 1Kh18N9T steel is more considerable.

Intensification of corrosion processes with the presence of carbon in lithium is possible for the following reasons. There is known the inclination of chromium-nickel steels to intercrystallite corrosion after heating in temperature range 500-800°C. With such heating from γ -solid solution there are separated excess carbides, which are distributed along grain boundaries (Fig. 7). Diffusion mobility of chromium is several orders lower than carbon; therefore, for formation of carbides chromium enters basically from volumes adjacent to grain boundaries. As a result of this boundary zones are significantly depleted by chromium, and at intense carbide formation the appearance of vacancies in these zones is inevitable.

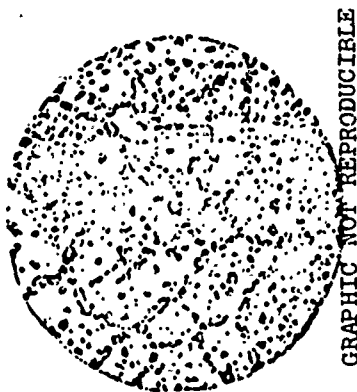


Fig. 7. Microstructure of 1Kh18N9T steel after aging in argon at 700°C for 200 h. Slide is not etched ($\times 1350$).

Analogous process occurs at contact of chromium-nickel steel with lithium, containing carbon impurities. Carbon, possessing higher chemical affinity to chromium than to lithium, diffuses from lithium into steel, which is indicated by appearance of radioactive isotope C^{14} in surface layers of samples. With entrance of carbon from lithium in surface layers of steel the process of carbide formation is strengthened, and zones of γ -solid solution, depleted by chromium, are saturated by vacancies (in addition to those vacancies which will be formed with solution zones of chromium-nickel steel).

Thus, with the presence of carbon in lithium there is intensified pore formation in surface zones of chromium-nickel steel, which, on the one hand, should considerably facilitate diffusion of chromium and nickel at the surface and their dissolution in lithium, and on the other - should cause more intense reduction of plastic properties. Finally carbon, proceeding from lithium into chromium-nickel steel, will affect the speed of corrosion process of steel. Furthermore, it is not excluded that atoms of chromium dissolved in lithium can participate in the formation of carbides directly in lithium. In this case impurities of carbon in lithium should cause additional depletion of surface of sample by chromium with all the consequences emanating from this.

Conclusions

1. Corrosional destruction of austenitic chromium-nickel steel at contact with lithium at 700°C is connected with decrease of content of chromium and nickel in surface layer, as a result of which in this layer there appears porosity, lowering the plastic properties of steel.
2. Impurities of carbon in lithium significantly affect the degree of corrosion of 1Kh18N9T steel in lithium, causing more intense lowering of concentration of chromium and nickel in surface layers.
3. Testing of chromium-nickel steel in reaction beakers from other material intensifies the processes proceeding with corrosion of steel in lithium.

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